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Factors Involved in the Stereochemistry of Diol Complexes

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A study has been made of the complexes formed by certain cyclic and bicyclic diols of known stereochemistry with boric acid and cuprammonium solution. The extent of complex formation has been measured in each case by conductometric methods. The results have been compared with infrared measurement of internal hydrogen bonding in these same substances. The significance that these observations hold for the structure and conformation of diols in general is also discussed.

The classical experiments of Böeseken and coworkers[2] have established that the near coplanarity of two vicinal hydroxyl groups is required for the formation of boric acid complexes. Diols, as emphasized in the reports of Reeves and co-workers,[3] also form complexes with Schweitzer's solution, the reaction taking place between cuprammonium ion and two suitably situated hydroxyl groups. Reeves, in fact, was able to specify[3b,d] that complex formation can occur when the projected angle[4] varies from 0° by no more than approximately 60°.

It was our purpose in the present study to examine closely the steric requirements for both boric and cuprammonium complexing in a number of cyclic and bicyclic diols and, if possible, to correlate the results with infrared hydrogen bonding measurement. It was hoped, thereby, to determine the extent to which these criteria could be used for analysis of steric factors determining the structure and conformations of cyclic systems.

Results and Interpretation

The Complexes of Vicinal Cyclohexane Diols.—Böeseken's[2b] demonstration of the failure of both *cis* and *trans* vicinal cyclohexanediols to enhance boric acid conductivity can be construed as evidence that the six carbon atoms of cyclohexane do not lie in one plane: an experimental proof of the Sachse–Mohr theory. In contrast to this (see Table I) cuprammonium solution shows a substantial conductivity decrement with both cyclohexanediols, the *cis* being slightly greater than the *trans*. Thus, the formation of cuprammonium complexes, where the corresponding boric complexes do not obtain, is at once an indication of the considerable disparity in steric requirements. Correlation is also evident with infrared hydrogen bonding measurements,[5,6] on these compounds. The greater $\Delta\nu$-value of I is considered indicative of a tighter hydrogen bond and, consequently, a shorter oxygen–oxygen bond distance. Kuhn[6] has on this basis calculated a projected angle of 50° for the *cis* as compared to 60° for the *trans*. The greater conductivity decrement of the *cis* is, therefore, in line with Reeves' prediction[3b,d] on the sole basis of the projected angle. Consequently, the present results serve to emphasize that a cuprammonium–diol complex is capable of existence in a puckered non-planar configuration whereas the boric–diol complex can sustain almost no departure from planarity.

Complexes with Vicinal Bicyclo[2.2.1]heptanediols and the Structure of Camphor Glycol.—In this regard we have attempted to explore the relative stability of complexes derived from diols with a projected angle of 0°. In earlier work[7] it has been shown by hydrogen bonding measurements that even in *cis* vicinal cyclopentanediol the projected angle is greater than 0°. The conductivity increment in boric acid, which is sharply in inverse proportion to the magnitude of the projected angle, is seen from Table I to be quite low, in consonance with that conclusion. In the two (III and IV) rigid, vicinal bicyclo[2.2.1]heptanediols the projected angle must be constrained to a minimum value, the same for both *endo* and *exo* isomers as indicated[7] by the $\Delta\nu$ estimate of the oxygen–oxygen bond distance. From Table I, we note the complete absence of correlation between the oxygen–oxygen distance and complex formation with both boric and cuprammonium. The *endo*-diol IV and the *exo*-diol III display almost identical $\Delta\nu$-values; but the *endo*-boric acid conductivity is scarcely greater than *cis*-cyclopentanediol, while the *exo*-acid has one of the largest values of Δ eq. recorded in saturated systems containing only carbon in the ring. Entirely parallel behavior is observed for cuprammonium; the *exo*-diol III forms a much more stable complex than the *endo* (Table I). Surprisingly, however, the extent of complexing of the *exo*-diol III with cuprammonium is only little greater than in the case of *cis*-cyclohexanediol (I).

Clearly, the (axial) transannular hydrogen atoms in the bicyclic ring exert a considerably greater destabilizing influence on the *endo* (IV) complex with both boric and cuprammonium ion. Even the methylene hydrogens on the bridge of the bicyclo [2.2.1.] ring tend to destabilize the *exo* (III) complex, as witness the comparison of the *exo*-diol cuprammonium complex of (presumably) 0° projection angle with the *cis*- and *trans*-cyclohexanediols of approximately 60° projection angle.

The sensitivity of complex stability to steric fac-

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[1] Part of this material was taken from the dissertation of G. C. Gatos, submitted in partial fulfillment of the requirements of the degree of Master of Science at the University of Delaware, June, 1956.

[2] (a) J. Böeseken, *Ber.*, **46**, 2612 (1913), *Bull. soc. chim.*, [4] **53**, 1332 (1933); (b) J. Böeseken and J. V. Geffen, *Rec. trav. chem.*, **39**, 186 (1920); (c) see also J. Böeseken, *Adv. in Carbohydrate Chem.*, **4**, 189 (1949).

[3] (a) R. E. Reeves and J. R. Jung, THIS JOURNAL, **71**, 209 (1949); (b) R. E. Reeves, *ibid.*, **71**, 212, 2116 (1949); (c) R. E. Reeves, *ibid.*, **73**, 957 (1951); (d) R. E. Reeves, *Adv. in Carbohydrate Chem.*, **6**, 109 (1951).

[4] The projection of the angle made by the two valence bonds onto a plane perpendicular to the carbon–carbon bond is called the projected angle between the groups under consideration; see reference 3d, p. 110.

[5] L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

[6] L. P. Kuhn, *ibid.*, **76**, 4323 (1954).

[7] H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954).

TABLE I

COMPLEXING AND INFRARED RESULTS ON CYCLIC AND BICYCLIC DIOLS

Compound	Boric acid, Δ^a equiv.	Cupra-ammonium, Δ^a equiv.	Hydrogen bond, cm.$^{-1}$ Free OH	Intromolec. bonded OH	
cis-Cyclohexane-1,2-diol (I)	0	−1.60	3626	3587	39[b]
trans-Cyclohexane-1,2-diol (II)	0	−1.44	3634	3602	32[b]
exo-exo-2,3-Dihydroxybicyclo[2.2.1]heptane (III)	2.37	−1.80	3632	3529	103[c]
endo–endo-2,3-Dihydroxybicyclo[2.2.1]heptane (IV)	0.38	−0.32	3633	3531	102[c]
exo–exo-2,3-Dihydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane; camphor glycol (V)	0	0	3626	3534	91
exo-2-*syn*-7-Dihydroxybicyclo[2.2.1]heptane (VI)	0	−0.97	3621	3545	76[c]
cis-2,8-Dihydroxybicyclo[3.2.1]octane (VII)	0	−1.11	3620	3520	100
cis-Cyclopentanediol (VIII)	0.30	....	3633	3572	61[b]
Trimethylene glycol (IX)	0	0	3636	3548	88[b]

[a] See Table II for definitions of these quantities. [b] Data taken from ref. 5. [c] Data taken from ref. 7.

TABLE II

CONDUCTIVITY OF DIOLS IN COMPLEXING SOLUTION AT 25°

Diol[a]	Specific conductance, ohms^{-1} cm.$^{-1}$ × 10^{-6} Boric acid (1)	Diol (alone) (2)	Diol in boric acid (3)	$\Delta^b(10^{-6})$	Δeq.[c]
III	27.9	51.7	674	594	2.37
IV	27.9	38.0	160	93.9	0.38
	Specific conductance, ohms^{-1} cm.$^{-1}$ × 10^{-3} Cupra solution (1)	Diol (alone) (2)	Diol in cupra solution (3)		
I	2.833	0.128	2.56	−400	−1.60
II	2.833	.068	2.54	−360	−1.44
III	2.833	.052	2.43	−460	−1.80
IV[d]	1.370	.027	1.32	− 77	−0.31
VI	2.833	.019	2.61	−240	−0.97
VII[e]	2.833	.039	2.73	−140	−1.10

[a] All diol concentrations were 0.250 *M*. [b] Defined as Δ = column (3) − Σ column (1) and column (2). [c] Defined as Δ eq. = (Δ/diol molarity)1000. [d] This measurement was made with solvent which contained 15% ethanol by volume. [e] Diol concentration here was 0.127 *M*.

tors is most extreme in the case of camphor glycol (V). This substance, which is readily obtained as the most stable product of reduction of camphor quinone,[8a,b] has been suggested[8c] to have the *exo–exo*-hydroxyl configuration largely on the basis of the analogous mode of reduction of camphor. Direct evidence to this effect, however, has been lacking. The complex formation evidence, taken in conjunction with the $\Delta\nu$ measured for the hydrogen bond confirms this assignment unequivocally. Thus, both boric acid and cuprammonium are completely unreactive in complex formation with camphor glycol yet the projection angle deduced from the hydrogen bond measurement is approximately 0°. If the hydroxyls were of the *endo–endo* configuration the same steric environment should prevail, arising from the non-bonded interaction of the transannular hydrogens that has been demonstrated (above) for the *endo-endo*-diol IV, and, therefore, complex formation with both boric and cuprammonium should have occurred to almost the same extent as IV (Table I). The steric effect of substituents on the bridge, which interferes considerably (as noted above) with the formation of the cuprammonium complex of III, is exaggerated to a decisive degree by the *gem*-dimethyl groups of V. The failure to observe complex formation by V is, therefore, consistent only with the *exo-exo* assignment for the structure of camphor glycol.

Reeves[3d] has correlated complexing with cuprammonium and acetonide formation in vicinal diols with some apparent success. However, camphor glycol (V) readily forms an isolable acetonide[14] and, consequently, its failure to show any complexing with cuprammonium is seen to be beyond the scope of this correlation.

Complex Formation with 1,3-Diols.—The literature[2c] on boric acid complexing does not report any corroborated instances of 1,3-diol complex formation. Cuprammonium complexing with 1,3-diols has received very little discussion, Reeves reporting[3a] that even trimethylene glycol belongs in the group of substances which fail to give a copper complex.[9] However, an extremely tight hydrogen bond signifying a short oxygen–oxygen distance is reported for this 1,3-aliphatic diol by Kuhn[5a] and *cis*-cyclohexane-1,3-diol exhibits a $\Delta\nu$-value (75 cm.$^{-1}$) indicative of a conformation in which the hydroxyl groups are erected in the (ordinarily unfavorable) axial positions. An even shorter oxygen–oxygen distance in a 1,3-cyclic diol is present in 2,7-norbornanediol (VI). As shown in Table I, boric acid failed to react with VI. Cuprammonium showed moderate activity, however, forming a less stable complex than II but one of far greater stability than IV. Apparently, in a system such as VI, where the spatial relationship between the hydroxyls is very rigidly maintained, a cuprammonium complex is readily formed; but, though oxygen–oxygen distance is minimized in this relationship and the projected angle can be construed as 0°, these are not alone the controlling factors. The failure of trimethylene glycol (IX) to complex may possibly be set down to the effect of forming an asymmetric ring which exerts a large rotational moment thereby producing instability. This effect is almost obliterated by the formation of the new ring upon a base as rigid as the bicycloheptane skeleton of VI. Further investigation of this fac-

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(8) (a) L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949); (b) H. Rupe and F. Müller, *Helv. Chim. Acta*, **24**, 265E (1941); (c) P. Hirsjärvi, *Ann. Acad. Sci. Fennicae*, **A1181**, 7 (1957).

(9) However, 1,3-complexing with methyl 3-methylidopyranoside (R. E. Reeves, THIS JOURNAL, **72**, 1499 (1950)) has been noted. Failure of 1,3-complexing with 3-methylidosan but formation of the analogous complex with 3-methyllevoglucosan have been reported in reference 3b.

tor is in progress in these laboratories, although other illustrations of the effect are already available.

Thus, the strength of the hydrogen bond in VII, which is seen to be an analogous 1,3-cyclohexanediol constrained by an ethano bridge across the 2,6-positions,[10] is somewhat surprising. The failure to form a boric acid complex (Table I) is not unexpected. The cuprammonium complex is seen to be slightly more stable than that of the 2,7-norbornanediol (VI) in accord with the somewhat smaller oxygen–oxygen distance.

As a general conclusion stemming from all the above considerations we have inferred that cyclic complex formation or the formation of fused ring compounds with conventional diol reagents must be used with considerable circumspection when applied for purposes of conformational analysis in cyclic diols. These limitations may very probably be attributed to changes in ring conformation, that in some cases very probably attend the formation of a new heterocyclic ring fused onto the carbocyclic base.

Experimental

Measurements.—A commercial 1000-cycle conductivity bridge was employed. The cell constant was 0.425, determined by the use of 0.1 *N* potassium chloride. For measurement of the conductivity of diol–boric acid complexes, unless otherwise specified in the data summaries, a 0.5 *N* boric acid solution in distilled water was used. The various quantities measured to determine the extent of complexing are listed and described in Table II.

For measurement of the conductivity of diol–cuprammonium complexes a suitable solution of Schweitzer reagent was prepared according to the method of Reeves.[3a] A current of air was passed through a mixture of copper turnings and concentrated, C.P. ammonium hydroxide contained in a tall cylinder and kept at 0°. The actual solution used contained 0.01 *M* copper, 3 *M* ammonia and 10 ml. of ethanol per liter. As usual, the decrease in conductivity of this cuprammonium solution on addition of diol is a measure of the extent of complexing. The measurements taken with the various diols are summarized in Table II.

Preparation of Compounds.—*trans*-**Cyclohexane-1,2-diol** (I) was made according to the procedure of Roebuck and Adkins[11] by oxidation of cyclohexene with performic acid; m.p. 104–105°.

cis-**Cyclohexane-1,2-diol** (II) was made by permanganate oxidation of cyclohexane at low temperatures according to the procedure of Clarke and Owen[12]; m.p. 98°.

exo–exo-**2,3-Dihydroxybicyclo(2.2.1)heptane** (III) was made by oxidation of norbornene with permanganate at low temperature according to the procedure in reference 7; m.p. 140–141°.

endo–endo-**2,3-Dihydroxybicyclo(2.2.1)heptane** (IV) was made by condensation of cyclopentadiene and vinylene carbonate according to the procedure in reference 7; m.p. 201–202°.

cis-**Camphor glycol** (V) was prepared by two methods. In both cases camphor (U.S.P.) was the starting material. (a) Camphor was oxidized by SeO_2 to camphor quinone[13] and the product of this reaction was reduced with lithium aluminum hydride according to the method of Trevoy and Brown.[8a]

(b) Camphor quinone[13] was reduced by zinc and acetic acid[7] to a hydroxy-camphor and this in turn was reduced by sodium amalgam to a mixture of the *cis*- and *trans*-glycols.[8b] The mixture was separated readily by formation of the *cis*-acetonide with acetone[14]; m.p. 253–255°.

exo-**2**-*syn*-**7-Dihydroxybicyclo(2.2.1)heptane** (VI) was made by oxidation of norbornene with performic acid according to the directions given in reference 7. The product was purified by several sublimations at approximately 120°. The product melted at 177–178°.

cis-**2,8-Dihydroxybicyclo(3.2.1)octane** (VII) was made by following the procedure of Walborsky and Loncrini[10] using the reaction of performic acid and bicyclo(2.2.2)octene-2; m.p. 255–257°.

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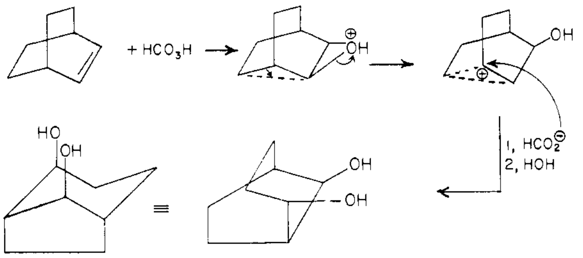
[10] The compound we are reporting has been assigned the structure of VII on the basis of a presumed Wagner–Meerwein rearrangement accompanying the addition of the elements of HOOH to bicyclo-(2.2.2)octene, analogous to the formation of the 2,7-diol VI when norbornene is treated with HCOOOH under similar conditions.



VII

This assignment is supported by a negative periodic acid test and a strong hydrogen bond determined by infrared measurements. H. M. Walborsky and D. F. Loncrini, THIS JOURNAL, **76**, 5396 (1954), have reported the formation of a *trans*-2,3-diol from this reaction.

[11] A. Roebuck and H. Adkins, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 217.

[12] M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 318 (1949).

[13] W. C. Evans, J. M. Rodgion and J. L. Simonsen, *ibid.*, 137 (1934).

[14] See reference 8b as well as H. Rupe and W. Tommen, *Helv. Chim. Acta*, **30**, 933 (1947).